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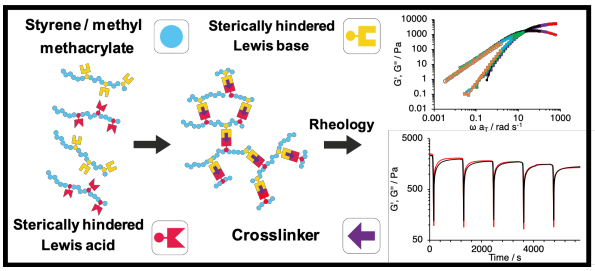
ABSTRACT

Conventional Lewis acids and Lewis bases will react with each other to form thermodynamically stable Lewis adducts which are inherently unreactive. Sterically encumbered Lewis acids and Lewis bases are prevented from forming such adducts, resulting in the formation of frustrated Lewis pairs (FLPs) with latent reactivity. Extending this concept to polymer science permits the development of a new class of responsive, functional, self-healing materials. Here, we report the

rheology of fully macromolecular FLPs based on both styrene and methyl methacrylate (MMA) backbones. When reacted with small molecule cross-linkers, a dynamic network is formed which is both heat-responsive and self-healing. The effect of polymer backbone and crosslinking density on the formed networks is significant. First generation polymeric FLPs behave in a similar way to the non-covalently linked supramolecular assemblies, where switching from styrene to MMA comonomers create stiffer polymer networks as the likelihood of chain entanglements increased with a more flexible backbone.



Introduction

Polymeric materials that can be reshaped, reprocessed and self-healed after damage have drawn particular attention as a class of smart materials. Such materials contain dynamic crosslinks, which enhance physical properties and respond to external stimuli, enabling reshaping/healing of the material via dynamic crosslinking exchange.[1] Compared to conventional, irreversibly crosslinked polymeric networks, dynamic crosslinking recovers the original physical parameters after a damage/healing cycle. There are many dynamic covalent bonds used as crosslinks in polymer networks, including carbon-carbon bonds based on reversible Diels-Alder[2] or cycloaddition reactions[3], boronic ester[4-6] or boroxine bonding,[7] siloxane bonds,[8] disulfide/thiol bond.[9] In addition, many supramolecular interactions have also been applied into this field of chemistry, including hydrogen bonds,[10] ionic bonds,[11] π-π stacking,[12-14] and Lewis pair complexation.[15]

Frustrated Lewis pairs (FLPs) were first disclosed by Stephan and coworkers in 2006.[16] Compared to conventional Lewis pair adducts, the Lewis acid (LA) and Lewis base (LB) in FLPs bear bulky groups which preclude themselves from binding to each other.[16-18] As a result, the LA and LB remain reactive and can activate many small molecules including alkenes,[19, 20] alkynes,[19, 21] cyclic ethers,[22] carbonyls,[18, 23] dihydrogen[24, 25] and carbon dioxide.[26-28] The activated small molecule can bridge between the LA and LB active centers, and in many cases providing dynamic and even reversible linkages under ambient temperatures. We recognized that this unique feature would launch a novel class of dynamic materials using FLPs as the linking sites.[29-33] In our first-generation system, we used polymeric FLPs as macromolecular network precursors with gelation triggered by the addition of a small molecule, diethylazodicarboxylate (DEAD).[29] The FLP crosslinks in our system appeared to be dynamic, producing a material that is temperature responsive and has the capacity to self-heal. Driven by these promising findings, we were motivated to explore the rheological properties of this novel new class of materials. Importantly, we also explored the impact of the nature of the comonomer on the performance of the poly(FLP) gels.

This article represents the first in deep study into the rheological properties of polymeric frustrated Lewis pairs. The macromolecular FLPs in this research were prepared by reversible addition-fragmentation chain transfer (RAFT) copolymerization of designer Lewis base/acid containing monomers with either styrene or methyl methacrylate (MMA) comonomers. The dynamic behavior of the crosslinks, explored using both rheological and spectroscopic analysis, paints a unique picture of the impressive potential of these first-generation poly(FLP)s.

Experimental

Materials – Styrene (Sigma-Aldrich, ≥99.5%), methyl methacrylate (Sigma-Aldrich, ≥99%), phosphorus trichloride (Sigma-Aldrich, 99%), 4-chlorostyrene (Alfa-Aesar, 99%), 2-bromomesitylene (Acros Organics, 99%) and deuterated chloroform (Sigma-Aldrich, 99.8% D) were dried over CaH_2 (Sigma-Aldrich, 95%), then distilled and degassed prior to use. Mg turnings (Sigma-Aldrich, ≥99.5%) were pre-heated in an oven at 200 °C for at least 2 days before use. Diethyl azodicarboxylate (Alfa-Aesar, 97%) was degassed, then dissolved in anhydrous toluene and dried with 3Å molecular sieves. Cumyl dithiobenzoate (CDB), 4-styryl-diphenylborane, 4-styryl-dimesitylphosphine, triphenylborane and 1,3,5-triisopropyl-2,4,6-trioxane were synthesized according to the literature procedures.[29, 34-36] Anhydrous diethyl ether, THF, toluene and hexane was obtained from an Innovative Technologies Solvent Purification System containing alumina and copper catalysts. All solvents were degassed prior to use by freeze-pump-thaw for three cycles. Anhydrous deuterated toluene was degassed and dried over 3Å molecular sieves. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Sigma-Aldrich, 98%) was purified by repeated recrystallization from methanol. 1,2-dibromoethane (Sigma-Aldrich, 98%), ammonium chloride (Alfa-Aeser, 98%), anhydrous magnesium sulfate (Fisher Scientific) and Fluorinert® (3M, FC-40) used as received.

Synthesis of 4-phenyl-dimesitylphosphine - Under an N_2 atmosphere, 1,2-dibromoethane (0.12 mL, 1.39 mmol) was added into a mixture of magnesium turnings (0.40 g, 16.5 mmol) and anhydrous THF (28 mL). The mixture was stirred for 30 min, and then bromobenzene (2.14 g, 13.6 mmol) was added dropwise across 45 min. After addition, the mixture was further refluxed for 30 min, and then stirred at r.t. for 1h to give a grey black Grignard solution. This Grignard solution was transferred dropwise *via* cannula into a THF solution (40 mL) of dimesitylphosphorus halide (3.60 g, 11.4 mmol) at 0 °C, prepared according to the published procedure.[29] After addition, the mixture was allowed to warm back to r.t. and stirred overnight. The reaction was then

quenched by addition of saturated NH_4Cl aqueous solution. The aqueous phase was extracted by Et_2O (50 mL × 3) and the combined organic phase was dried over $MgSO_4$. After removal of solvent under reduced pressure, the crude product was purified by column chromatography (hexane) to give a white solid (1.60 g, 40.6%).

Copolymerization with styrene – Pre-weighed amounts of styrene, cumyl dithiobenzoate, 1,3,5-triisopropyl-2,4,6-trioxane (internal standard) and 4-styryl-diphenylborane or 4-styryl-dimesitylphosphine were mixed together under N_2 atmosphere. A small amount of toluene was added to improve solubility of the Lewis acid/base monomer to a final concentration 7.4 M. A small aliquot of the solution was collected and analyzed by ^1H NMR ($CDCl_3$) spectroscopy. The remaining solution was transferred into an ampoule and sealed under an inert atmosphere. The mixture was heated to 110 °C for 45 hours. The polymerization was then terminated by cooling the resultant sticky mixture to r.t. after which a small aliquot was collected for ^1H NMR ($CDCl_3$) analysis. The mixture was diluted with a small amount of dry toluene, then precipitated twice into anhydrous hexane under N_2 atmosphere. Filtration and subsequent drying under vacuum isolated the copolymer product as a pink powder.

Copolymerization with MMA - Pre-weighed amounts of MMA, cumyl dithiobenzoate, 1,3,5-triisopropyl-2,4,6-trioxane (internal standard), AIBN and 4-styryl-diphenylborane or 4-styryl-dimesitylphosphine were mixed together under N_2 atmosphere. A small amount of toluene was added to improve solubility of the Lewis acid/base monomer to a final concentration 5.7 M. The solution was transferred into an ampoule and sealed under inert atmosphere. The mixture was heated to 70 °C for 18 hours. The polymerization was then terminated by cooling the resultant sticky mixture to r.t. after which a small aliquot was collected for ^1H NMR ($CDCl_3$) analysis. The mixture was diluted with a small amount of toluene, then precipitated twice into hexane under N_2

atmosphere. The copolymer product was obtained as a pink powder by filtration and dried under vacuum.

Network Formation - Phosphorus- and boron-containing copolymers were dissolved into anhydrous toluene with 1:1 equivalent of boron and phosphorus moieties under N_2 atmosphere. Diethyl azodicarboxylate (5 equivalents) from stock solution (0.63 M) was quickly injected into the solution. The total concentration of the solution was kept constant at 0.02 moles of FLP units per dm^3 after the addition of DEAD solution. The mixture was allowed to stand at ambient temperature overnight. In the event of gel shrikage, the upper clear solution was decanted off prior to any analysis.

Rheology - The mechanical properties of polymeric frustrated Lewis pair gels were analyzed by using a stress-controlled Anton Paar MCR302 rheometer with a 40 mm diameter crosshatched tool at 1 mm gap. All tests were performed under air, after gels were cycled out of the inert atmosphere. The 50 mm diameter bottom plate was likewise crosshatched, and edges of the gels were covered with inert fluorinated oil (3M, FC-40) to prevent the evaporation of toluene from the gel. Oscillatory frequency sweeps were performed at 0.1% and 1% strain for 4% and 7% crosslink density gels, respectively, ensuring that both types of gels remained in the linear viscoelastic regime. The frequency range for those experiments was from 0.1 rad s^{-1} to 100 rad s^{-1}. Amplitude sweep tests were performed at 30 rad s^{-1}, where all the gels behaved as viscoelastic solids and strain was increased from 0.01% to 400%. Recovery tests were performed at 30 rad s^{-1}, with up to 80% strain as this was determined to be enough to yield all the gels. This was followed by a recovery period where the strain was reduced to 0.1% or 1%, depending on the crosslink density, and the recovery of the moduli was recorded over 5 to 30 minutes. Temperature sweeps from 0 °C to 50 °C were performed at 30 rad s^{-1} and 0.1% or 1% strain with a heating rate of 0.05 °C s^{-1}.

Results and Discussion

To synthesize polymeric frustrated Lewis pairs, styrene-based Lewis acidic and Lewis basic monomers (**I** and **II**, Scheme 1) were synthesized as previously reported by our group.[29] These monomers were separately copolymerized with styrene and MMA via RAFT polymerization[37, 38] to yielding polymers containing sterically crowded Lewis acids, poly(sty-co-LA) and poly(MMA-co-LA), and sterically crowded Lewis bases, poly(sty-co-LB) and poly(MMA-co-LB), as shown in Scheme 1. CDB was selected as the RAFT agent as it enables well-controlled polymerizations of styrene and methyl methacrylate and it was found not to be able to bind with the Lewis acidic borane monomer (**I**) at both ambient and polymerization temperatures. These first polymeric FLPs reported were based on styrene.[29, 30] However, as polystyrene is a hard and inflexible polymer, we wanted to contrast these with a classically more flexible backbone, poly(methyl methacrylate).[39] We wondered whether the change from styrene to methyl methacrylate would bring some flexibility to the polymer backbone, as this would enable finer dynamic rearrangement of the polymer chains during the crosslinking process. The copolymerizations of **I** and **II**, separately, with styrene were performed at 110 °C. The conditions were slightly modified to 70 °C for the copolymerizations with MMA since self-initiation with this comonomer would result in uncontrolled polymerizations. The radical initiator AIBN was used in these copolymerizations, as it was found not to affect the gelation as it was not found to be able to bind to the borane monomer in the NMR spectroscopy studies. Different loadings of **I** and **II** in copolymers were targeted to understand the effect of the crosslinking density on the resulting gels. The results of the copolymerizations are shown on Table 1.

Scheme 1. RAFT copolymerizations of 4-styryl-diphenylborane, **I**, and 4-styryl-dimesitylphosphine, **II**, with styrene and MMA, separately. Conditions, a and c – CDB, 110 °C; b and d – CDB, AIBN, 70 °C.

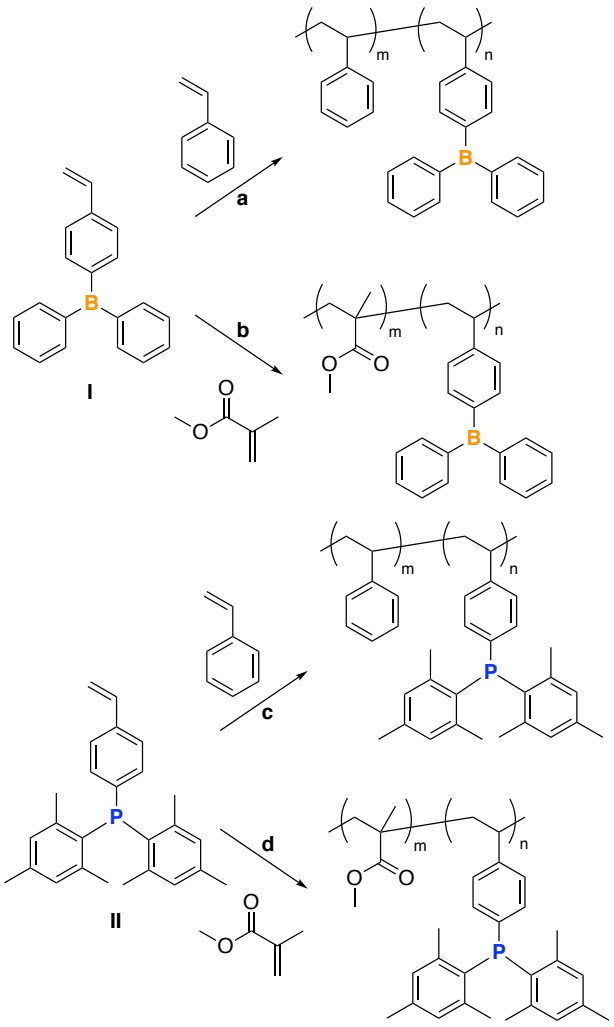


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Table 1. Polymers obtained by the RAFT copolymerizations of styrene or MMA with 4-styryl-diphenylborane or 4-styryl-dimesitylphosphine. M_n (GPC) values were determined by using triple detector calibration constructed by using very narrow polystyrene standards. The *dn/dc* values used were 0.185 ml/mg and 0.088 ml/mg for the styrene and MMA-based copolymers, respectively.[40]

Entry No	Polymer	Feeding Ratio				Conversion / %		M_n (theo)	M_n (GPC)	Dispersity
		sty/MMA	LA/LB	CDB	AIBN	sty/MMA	LA/LB	/ g mol^{-1}	/ g mol^{-1}	
1	Poly(sty-co-LA) 1	97	3	0.35	-	65	96	20800	24000	1.2
2	Poly(sty-co-LA) 2	95	5	0.32	-	51	93	19300	20000	1.2
3	Poly(sty-co-LB) 1	97	3	0.35	-	62	96	21900	25000	1.1
4	Poly(sty-co-LB) 2	95	5	0.35	-	60	94	26900	26000	1.1
5	Poly(MMA-co-LA) 1	98	2	0.35	0.14	70	97	21300	29000	1.3
6	Poly(MMA-co-LA) 2	95	5	0.35	0.14	62	94	21400	26000	1.2
7	Poly(MMA-co-LA) 3	92	8	0.35	0.14	57	88	20900	33000	1.2
8	Poly(MMA-co-LB) 1	97	3	0.35	0.14	72	96	23400	37000	1.6
9	Poly(MMA-co-LB) 2	95	5	0.35	0.14	75	94	25300	36000	1.3
10	Poly(MMA-co-LB) 3	92	8	0.35	0.14	76	90	28700	54000	1.3

Electron-donating or withdrawing substituents on a styrene-based monomer can lead to inductive effects that stabilize the transition states of polymerization propagations.[41] Therefore, both monomers **I** and **II** likely favor cross-propagation. This is confirmed from the polymerization conversion results shown in Table 1. In general, reasonably low dispersity values were obtained, suggesting controlled polymerizations. However, the copolymerizations with low loadings of **I** and **II** had higher dispersity values suggesting the possibility of some non-homogeneity, as some chains would potentially not contain any borane and phosphine monomers. A good agreement between theoretical and experimental number-average molecular weights (M_n) was observed for polystyrene copolymers. However, MMA-based macromolecular FLPs showed significant disagreements in these values. It is likely that bulky aryl-substituted Lewis acidic and Lewis basic monomers disrupt the organization of the MMA polymer chains in solution, resulting in different hydrodynamic volumes. In addition, GPC analysis was performed by using the *dn/dc* value known for polymethyl methacrylate (0.088 ml/mg in THF),[40] while the observed *dn/dc* values have large discrepancy with that of pure PMMA. The discrepancy between theoretical M_n and GPC measured

values increases with the borane/phosphine content, supporting this hypothesis. An exemplar *dn/dc* value was calculated for the 7 mol% phosphine containing copolymer, changing from 0.088 ml/mg to 0.103 ml/mg. Further information about the determination of this value is provided in SI, Section B.

Table 2: Details of the polymer networks prepared by the addition of a crosslinker into the mixture of two copolymers.

Polymer Network	Polymers (Entry No)	Crosslinking / mol%	Average number of crosslinking units per polymer	M_e / g mol^{-1}
Poly(sty-co-FLP) 1	1 and 3	4	7	79000
Poly(sty-co-FLP) 2	2 and 4	7	12	48000 - 31000
Poly(MMA-co-FLP) 1	5 and 8	4	7	-
Poly(MMA-co-FLP) 2	6 and 9	7	14	6000 - 10000
Poly(MMA-co-FLP) 3	7 and 10	11	22	-
Poly(sty/MMA-co-FLP)	4 and 6	7	13	6000 - 9000

Crosslinking of the poly(FLP) gradient copolymers was performed using the aforementioned azo compound DEAD as a crosslinker. Phosphorus and boron containing copolymers were mixed in dry toluene with 1:1 equivalent of borane and phosphine moieties. We note that the concentration of the toluene solution after DEAD addition is an important variable to this gelation, and we used a concentration of 0.02 M of FLP moieties (i.e. controlling the concentration of boron and phosphorus atoms in solution rather than total polymer) in all gelation experiments. The origin of this cross-linking reaction is the nucleophilic attack of the phosphine monomer to the N=N double bond, increasing the nucleophilicity of the second nitrogen (Figure 1 A) which is then free to interact with the boron center. Upon injection of DEAD into the copolymer solution (Figure 1, B1) a kinetically frustrated state of the polymer chains is quickly formed. This is followed by the rearrangement of the polymer chains to reach to a more thermodynamically stable state, often leading to gel shrinkage and expulsion of solvent. The gel can be reshaped as shown in Figure 1,

B4. A series of polymer networks were prepared by using the synthesized macromolecular FLPs as shown on Table 2. We have prepared 4 mol% and 7 mol% crosslinking poly(sty-co-FLP) networks and 4 mol%, 7 mol% and 11 mol% crosslinking poly(MMA-co-FLP)s networks based on the in-chain ratio of monomers. At higher cross-link densities gels do not form and instead precipitation of a network polymer is favoured in both styrene[29] and MMA based FLPs.

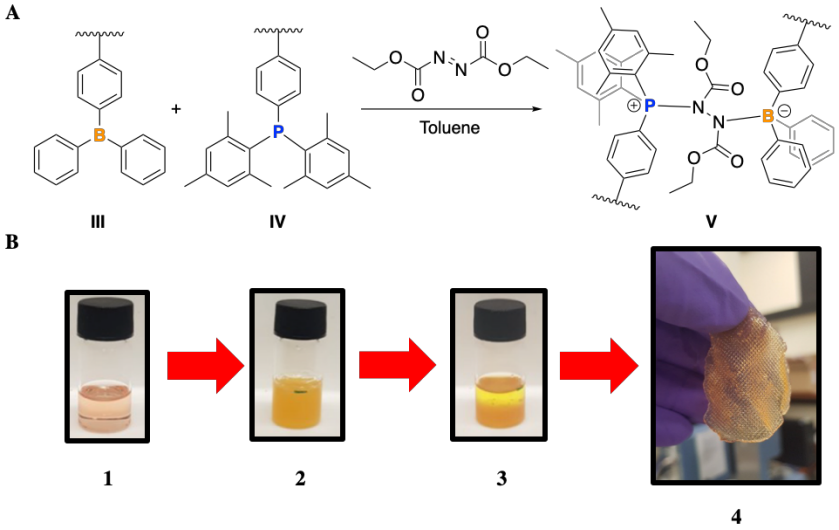

Figure 1. The crosslinking reaction which results in the formation of polymeric frustrated Lewis pair gels (A) and the visual changes that happens throughout the gelation (B); 1) a mixture of the copolymers is dissolved in toluene, 2) addition of DEAD results in an immediate change from solution to gel, 3) the gel shrinks to a smaller size as a result of the arrangement of the polymer chains arising from the dynamic nature of the crosslinking and 4) the resulting gel is reshaped and analyzed by a rheometer.

Dynamic mechanical properties of polymeric frustrated Lewis pair networks were investigated using oscillatory rheology. Results are shown for the 4 mol% crosslinking poly(sty-co-FLP) network in Figure 2, with similar behaviors observed in other poly(FLP) networks explored here (see Figure S4 and Figure 4D for more examples). Under small amplitude oscillatory shear, the frequency dependent storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, characterize the elastic (solid-like) and viscous (liquid-like) material response. These are shown for 4 mol% crosslinking

poly(sty-co-FLP) in Figure 2 (A). At high frequencies the storage modulus dominates, $G' > G''$, implying most of the deformation energy is stored elastically over short timescales, while at low frequencies the loss modulus dominates, $G'' > G'$, implying most of the energy is dissipated through relaxation of the polymer chains over longer timescales. The crossover frequency, ω_c, is defined by the condition $G'(\omega_c) = G''(\omega_c)$, and for this particular poly(FLP) network ω_c = 19 rad s^{-1} at 20 °C. The moduli can be fitted by a single-mode Maxwell model,

$$G'(\omega) = G_0 \cdot {(\omega/\omega_c)^2}\Big/{1 + (\omega/\omega_c)^2}$$

$$G''(\omega) = (\omega/\omega_c)G'$$

with G_0 = 3800 Pa.[42, 43] This single-mode behavior is typically observed in worm-like micelles, and also has been observed in polymeric supramolecular assemblies, such as hydrogen-bonded polymers.[44, 45] The plateau modulus should scale as $G_0 \propto \nu k_B T$, where ν is the number density of strands contributing to the elastic network, while the relaxation rate depends on the timescale for bond dissociation.[42, 46]

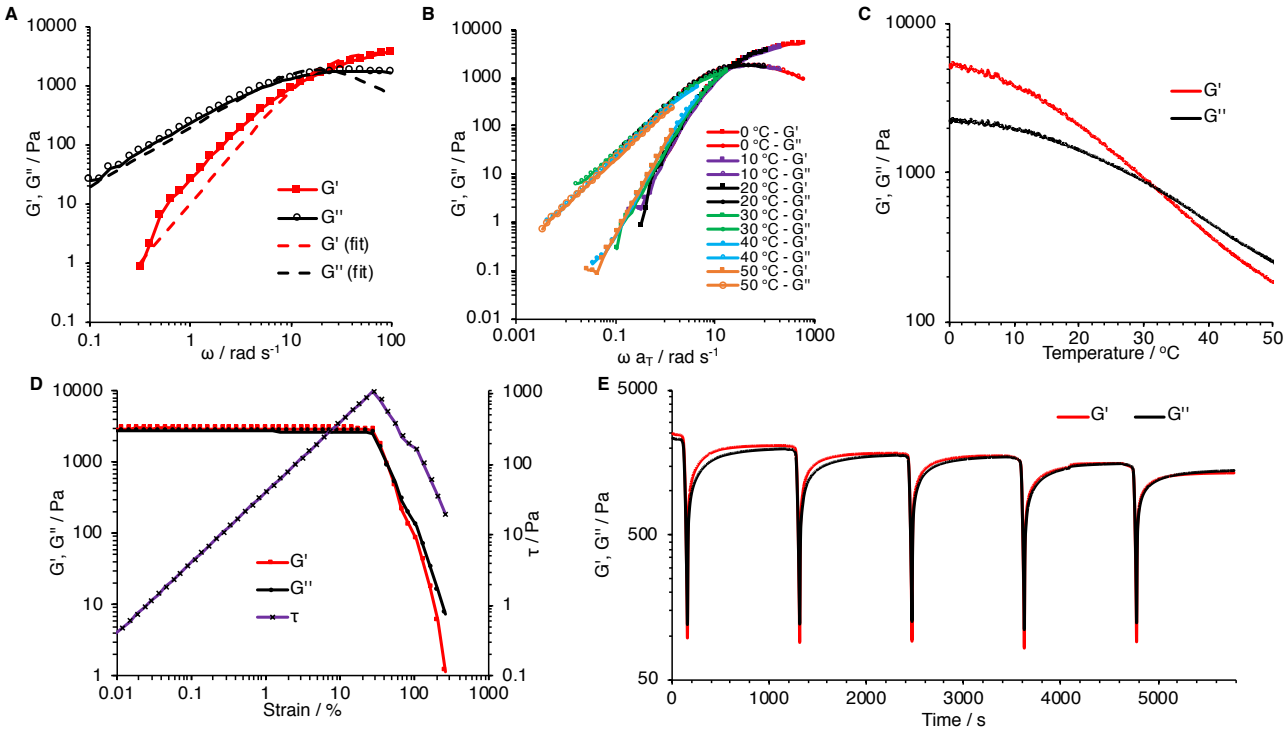

Figure 2. Dynamic mechanical properties of 4% crosslinking poly(sty-co-FLP) obtained by oscillatory rheology. Frequency dependencies of the dynamic moduli of the polymer network at 20 °C, 1% strain and theoretical fit obtained by using the Maxwell model (A), ω_c = 19 rad s^{-1}, G_0 = 3800 Pa, time-temperature superposition at the reference temperature 20 °C (B), temperature dependencies of the dynamic moduli G' and G'' at 30 rad s^{-1}, 1% strain at a heating rate of 0.05 °C s^{-1} (C), oscillatory amplitude sweep test showing how dynamic moduli and shear stress behaves as a function of strain (D) and the recovery of G' and G'' after failure induced by shear strain (E). The polymeric gel was sheared to failure under increasing oscillatory strain followed by a recovery under 1% strain.

We repeated small amplitude frequency sweeps at different temperatures from 0 °C to 50 °C (SI Figures S5-9). Above 50 °C, even with the oil seal, toluene would rapidly evaporate and dry out the gel. While the frequency dependent moduli changes with temperature in absolute terms, curves at different temperatures can all be collapsed onto a master curve using Time-Temperature Superposition (TTS), (Figure 2 (B) and Figure S10).[46] This collapse is achieved by rescaling the absolute frequencies, $\omega \rightarrow a_T\omega$, where a_T is a temperature-dependent shift factor relative to a reference temperature. The shift factor decreases with increasing temperature and a plot of log a_T vs temperature is provided in Figure S11. As the poly(FLP) gels obey TTS, it can be inferred that

they do not undergo any phase transitions or significant structural changes over this temperature range (0 °C to 50 °C). The master curve can again be fitted with single-mode Maxwell model, and the frequency shifts reflect a decrease in the relaxation timescale, $t_c(T) = 1/\omega_c(T)$, with increasing temperature. This is frequently observed in supramolecular gels formed from solutions of associating polymers,[47] where the network contains a number of non-covalent interactions with finite lifetimes.[48]

We further probed this temperature dependence, recording $G'(T)$ and $G''(T)$ at a fixed frequency, ω = 30 rad s^{-1}, as the temperature was slowly increased from 0 °C to 50 °C (Figure 2 C). The results are consistent with our TTS shifted master curve, with both moduli decreasing as the temperature increases, and ultimately crossing at 32 °C. Using the fact that the storage and loss moduli in a single mode Maxwell model are simply related by $G' = \omega t_c G''$, we estimate the temperature dependence of the relaxation time $t_c(T) = G'(T)/\omega G''(T)$. In general, relaxation of the polymer network involves contributions from segmental motion of the long polymer backbones, reptation, (t_r) and dissociation (t_d) times of the crosslinks.[49, 50] If the timescale for breaking crosslinks is sufficiently fast ($t_d << t_r$), the relaxation dynamics can be characterized by a single relaxation time corresponding to a first order or pseudo-first-order reaction rate $k_{obs} = 1 / t_c$.[42] Fitting our results to an Arrhenius equation $k_{obs}(T) = k_0 e^{-E_a/RT}$, it is possible to relate k_{obs} to the activation energy (E_a) for this process (Figure S12), calculated as 18.2 kJ mol^{-1}. This relaxation time, and thus also E_a, characterize the combined timescales for reptation and dissociation. This low value of E_a is realistic for a reversible process.[42]

The significant effect of the temperature suggests that the interaction between the anion and boron center is truly dynamic. An NMR spectroscopy experiment was designed to observe this interaction. Model compounds 4-phenyl-dimesitylphosphine and triphenylborane were

synthesized to mimic the interactions of polymeric FLPs. These molecules were mixed with one equivalent of DEAD and the interaction between the borane center and the nitrogen anion monitored at different temperatures by NMR spectroscopy (Figure 3). As temperature increases, the diagnostic resonance (ca. 1 ppm) decreases in intensity, accompanied by the formation of free triphenylborane (ca. 67 ppm) at high temperatures. These results confirm the temperature dependency of the interaction and its highly dynamic nature.

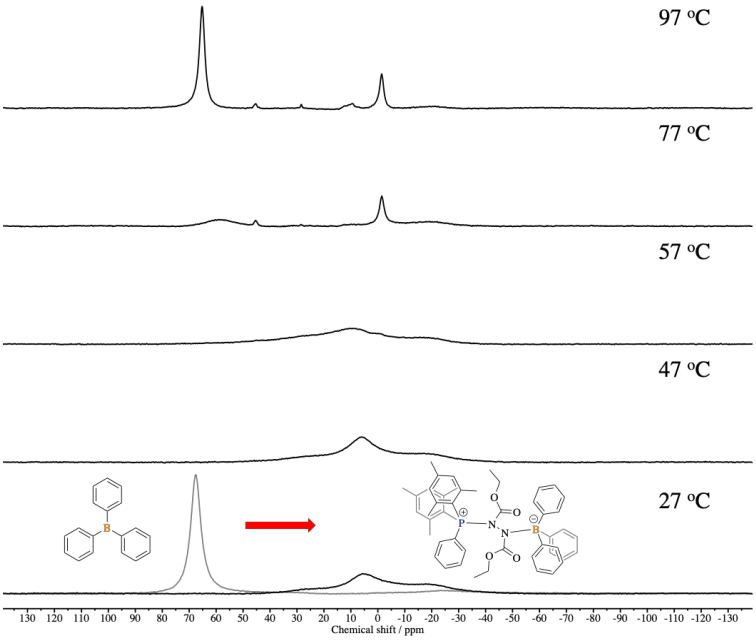

Figure 3. ^{11}B NMR spectra to demonstrate the effect of temperature on the crosslinking. Model compounds, triphenylborane and 4-phenyl-dimesitylphosphonine, were synthesized and linked by using 1 equivalent of DEAD in anhydrous toluene-*d8*. Variable temperature NMR experiments were performed from 27 °C to 97 °C.

Performing an amplitude sweep at 30 rad s^{-1}, where the polymer network behaves as a viscoelastic solid, we find that G' and G'' remained constant up to a yield strain around 28%.

Beyond this linear viscoelastic region, the material suddenly yields, with a rapid drop in the moduli and a decrease in the applied stress. This sudden stress drop, occurring at a yield stress of 1050 Pa, suggests the sudden fracture of the network, possibly due to degradation of non-crosslinked chains or dissociation of noncovalent bonds. Relatively low yield strains, here $\gamma_y \sim 28\%$, have been reported in other supramolecular polymer gels.[48]

In our previous report, we showed that polymeric frustrated Lewis pair gels can self-heal.[29] In this study, we further probe the self-healing properties of our polymeric system. We performed a series of shear amplitude sweeps, increasing the strain from 1% to 80% over 160 s to yield the gels, then recording the recovery of the moduli with time at a fixed 1% amplitude.[51] Results for a 4 mol% crosslinking poly(sty-co-FLP) are shown in Figure 2 (E). As the shear amplitude is increased beyond the yield strain G' and G'' decreased significantly, but after the strain returns to the linear viscoelastic region, network reconstitution began instantaneously. The gel recovers nearly all of its former strength roughly 15 mins after each yielding step. On average, 89% and 91% recoveries were observed after each yielding step for G' and G'', respectively, demonstrating repeatable self-healing in these poly(FLP) gels after damage.

Having synthesized a variety of copolymers, we explore how a change in crosslink density and polymer backbone affect the mechanical properties of our supramolecular polymeric gels. To examine the role of the crosslink density, poly(sty-co-FLP) gels with 4 mol% and 7 mol% crosslink densities were prepared by using the pairs **1**, **3** and **2**, **4** from Table 1. Comparing frequency sweeps at 20 °C for the two gels (Figure 4 A), we find that the crossover frequency shifts to a lower frequency with an increase in crosslinking density, along with a concomitant increase in the magnitude of the moduli. The decrease in ω_c with crosslinker density, corresponding to an increase in relaxation time t_c, has been previously observed in polymeric supramolecular assemblies.[43] This

increase in relaxation time could reflect either the need for multiple simultaneous bond breakages to effectively free chains or an increase in the reptation time as the polymer network becomes increasingly restrictive. Comparing strain amplitude sweeps with the two gels (Figure 4 B and C), we find a higher yield stress in the higher crosslink density gel, but a similar yield strain, $\gamma_y \sim 20\%$.

From the plateau modulus and the polymer concentration c, we can estimate the molecular weight between effective entanglements, M_e, using $G_0 = \frac{cRT}{M_e}$ (Table 2). In gels with higher crosslinking densities, phase separation and gel shrinkage make it challenging to accurately determine the polymer concentration c. This is both due to the variable polymer concentration in the discarded solvent, and also solvent-rich regions that tended to remain in the vial after loading the gel into the rheometer. In these gels, a range of M_e is provided, reflecting this uncertainty. The values obtained here, 79 kg/mol and ~40 kg/mol for 4% and 7% crosslink densities respectively, are larger than the molecular weights of the individual polymer chains, indicating a relatively low density of effective crosslinks. The decrease in M_e with increasing crosslinker concentration reflects an expected increase in the density of network junctions with an increasing number of reversible FLP bonds between chains.

We have demonstrated that these polyFLP networks exhibit numerous rheological features found in supramolecular physical gels formed by associating polymers in solution, reflecting the role of the reversible, non-covalent FLP bonds. The low density of effective crosslinks, along with the approximate agreement with a single-mode Maxwell model, indicates that these networks can be reasonably well-described by either Edwards transient network model[52] or wormlike-micell-inspired models[44, 53]. This is in contrast to behavior typically observed in associative polymer melts[50], which are instead frequently modeled with a 'sticky Rouse' model describing the hindered reptation of polymers with multiple binding sites per chain[54, 55].

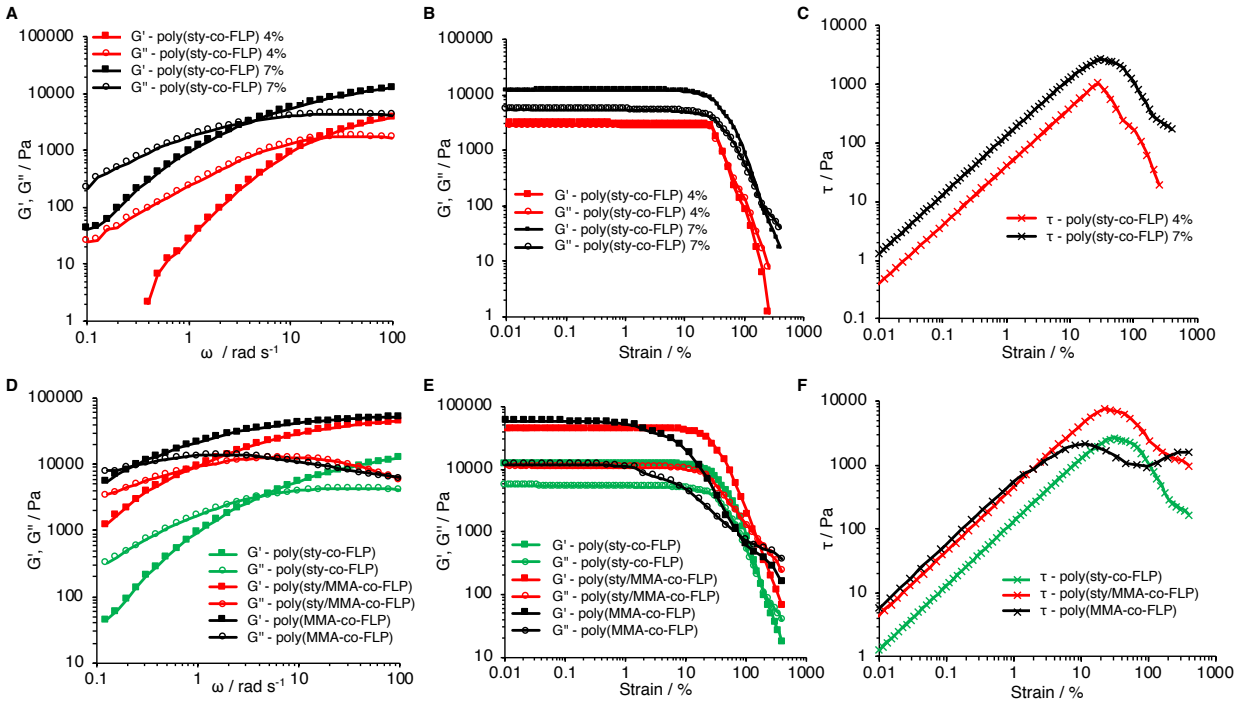

Figure 4. Plots of changes in crosslink density and polymer backbone vs. the dynamic mechanical properties of the polymeric frustrated Lewis pair gels. Frequency (A, D) and amplitude (B, C, E, F) sweep tests are shown above to describe these systems. Plots A, B and C show the effect of changing the crosslink density from 4 mol% to 7 mol% on styrene-based polymeric FLP gel whereas the plots D, E and F show the effect of polymer backbone where three different gels were prepared and reported, one based on PMMA, one based on PS and other a mixture of the two polymer backbones, all with 7 mol% crosslinking.

To investigate the role of the polymer backbone, gels were prepared at 7 mol% crosslink density with the following pairs of copolymers **2**, **4** (both styrene) and **6**, **9** (both MMA) and **6, 4 (**mixed styrene-MMA**)**. Theoretical molecular weights of the copolymers are similar, suggesting that any behavioral differences would be dominated by the change of backbone. Frequency sweeps were run on all resultant gels at 20 °C (Figure 4 D). The crossover frequency was lowest in the poly(MMA-co-FLP) gel and highest in the poly(sty-co-FLP) gel, with the mixed poly(sty/MMA-

co-FLP) gel falling in between, indicating a longer relaxation time with the more flexible MMA backbone. The gels with the MMA backbone exhibited a higher plateau modulus G_0, translating to a significantly lower molecular weight between effective entanglements, with M_e dropping from ~ 40 kg/mol with the styrene backbone to ~ 8 kg/mol with the MMA backbone. This drop occurs in spite of the higher molecular weight of the MMA polymers (Table 1). This indicates that the more flexible backbone actually results in a more solid-like gel by allowing the formation of more crosslinks.

To investigate the yielding behavior with different backbones, we carried out strain sweeps on these different gels (Figure 4 D and E). We found that networks formed with MMA containing copolymers resulted in a more brittle gel structures, as poly(MMA-co-FLP), poly(sty/MMA-co-FLP) and poly(sty-co-FLP) gels yielded at 1%, 22% and 28% strains, respectively. The yield stresses of both the MMA- and styrene backbone gels were comparable, ~ 2 kPa, but with the mixed backbone the yield stress increased to ~ 10 kPa.

Carrying out small amplitude frequency sweeps with the mixed backbone poly(sty/MMA-co-FLP) 7 mol% crosslinking networks, we find that these mixed backbone gels also obey the time-temperature superposition (Figure 5 and Figures S13-16). However, at high frequencies there are notable deviations from single-mode Maxwell behavior, with G'' flattening to a plateau instead of decaying as ω^{-1}. Deviations from simple single-mode dynamics at high frequencies are generally observed in supramolecular physical gels, and are generally ascribed to new relaxation modes beginning to enter the dynamics[42, 47]. Deviations at high frequencies are also present in even the 4% crosslinker styrene-backbone gels (Figure 4A), but are much more apparent in these MMA-backbone gels. In these gels, it is likely that the higher density of crosslinks likely begins to complicate the network relaxation dynamics.

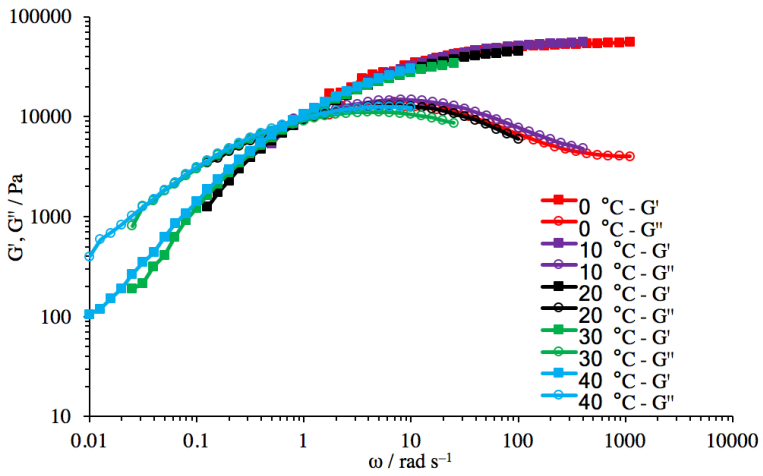

Figure 5: Time-temperature superposition master plot of frequency dependencies of the dynamic moduli of the 7 mol% crosslinking mixed sty/MMA based polymeric FLP network at a reference temperature of 20 °C.

Following the yielding behavior of the 7 mol% polymer networks, we wondered how a change in crosslink density and backbone would affect the self-healing properties of the gels. Recovery results similar to the 4 mol% poly(sty-co-FLP) network were obtained. As shown in Figure 6, the gels quickly healed themselves upon the removal of strain. 91%, 90% and 86% recoveries were observed for the 7 mol% crosslink density poly(sty-co-FLP), poly(sty/MMA-co-FLP) and poly(MMA-co-FLP) polymer networks, respectively. These values were obtained in 15 minutes, proving the fast healing characteristic of the poly(FLP) gels. Notably, there remained a positive healing trend when the experiment was terminated, suggesting potential full recovery over longer healing times. However, as toluene in the gels can evaporate, this could also cause an increase in G' and G" values and thus we purposely kept healing experiments short to mitigate this influence. The results are in line with the previously reported self-healing results with the networks formed by reversible crosslinks.[51, 56] We note that any decrease in the gel stiffness could arise from the hydrolysis of the borane units in the polymer networks. All rheology experiments were performed in air with a humidity up to 46%, giving potential for hydrolysis of the borane units within the

polymer networks. These borane units are susceptible to water in the air as once they are not protected by DEAD, i.e. during rearrangement / shearing. It is possible that every time some borane units are lost, and the number of crosslinks decreases.

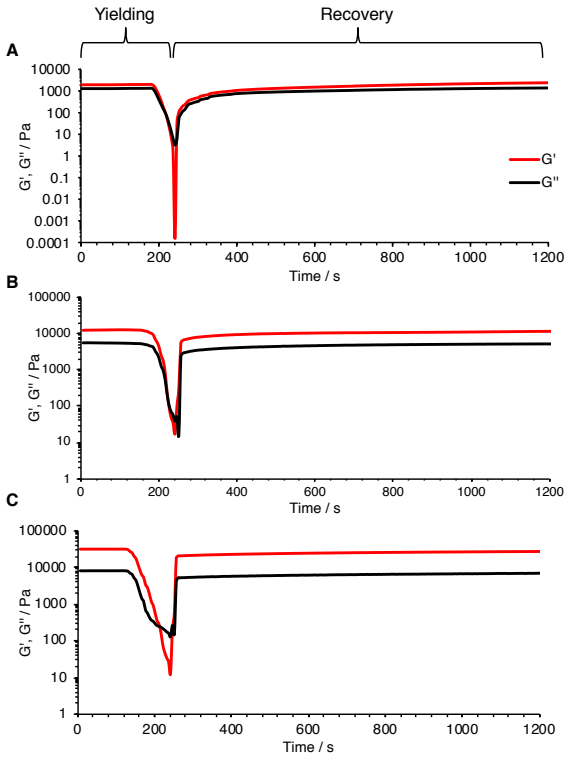

Figure 6: Self-healing properties of the gels with 7 mol% crosslinking (**A**) poly(sty-co-FLP), (**B**) poly(sty/MMA-co-FLP) and (**C**) poly(MMA-co-FLP) polymer networks. The gels were exposed to a stain value of 400% and the recovery of G' and G" was recorded after the failure. The experiment was performed at 30 rad s^{-1} over 1200 seconds.

Conclusion

A variety of copolymers with either sterically encumbered Lewis acid or Lewis base pendant functional groups were synthesized and activated using a small molecule, DEAD, resulting in dynamically crosslinked network structure. Rheological behavior of the resulting polymer networks showed that the networks behave as non-covalently linked supramolecular assemblies with a high temperature dependence. The crosslinking was shown to be highly dynamic. The self-healing behaviors of the gels were characterized, and the healing is fast and happens almost

immediately after the removal of yielding strain. The network structure breaks at relatively low strains, a characteristic of supramolecular assemblies. Poly(FLP) gels were understood to obey the time-temperature superposition suggesting that no change happens in the microstructure of the polymer network. It was demonstrated that an increase in crosslink density resulted in an increase in the likelihood of entanglements, resulting in a more solid-like material. A switch in polymer backbone from inflexible styrene to relatively more flexible MMA units results in easier chain rearrangement and crosslink exchange, where the material was almost solid-like at all frequencies analyzed. We believe that the combination of rich chemistry of FLPs with known activations of small molecules, such as H_2, CO_2, N_2O, alkenes and imines, and wide range of synthetic materials available through altering macromolecular backbone and architecture, such as blocks, stars and surfaces, promises a whole new class of novel stimuli-responsive materials with potential applications including CO_2 capture and catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Contents of SI:
Additional rheological and analytical characterization
Determination of *dn/dc* value for the poly(MMA-co-LB)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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